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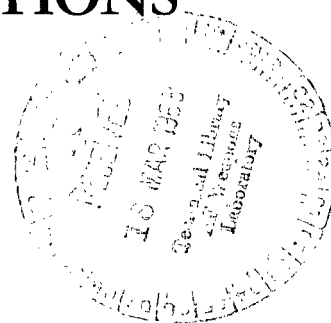


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# LATTICE STRUCTURES IN SOLUTIONS

*by Joseph S. Rosen*

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Huntsville, Ala.*





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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# LATTICE STRUCTURES IN SOLUTIONS

## SUMMARY

The concept of an irregular and random arrangement of ions in solution is rejected in this report. The interionic distances of the crystal lattice structure, assumed to be retained in solution, are maintained by the equilibrium between cohesive and repulsive forces on the ions in solution. This concept of a lattice structure in solution may have an important relation to the theory of an ionic atmosphere in electrolytic solutions.

Calculations are presented for various concentrations of the alkali halides; for concentrations when no water is present, the interionic distances for the alkali halides agree with results obtained by other methods.

## INTRODUCTION

This examination of the lattice structure of salts in solution is based on Masson's [1] empirical relation, or modifications of this relation. Masson's equation is

$$\Phi = \Phi_0 + S_c^{1/2} \quad (1)$$

where

$\Phi$  = apparent molal volume of the solute [the specific apparent volume (or apparent volume per gram),  $\phi$ , of a salt in an aqueous solution is defined by the equation  $v_s = x_1 v_w + x_2 \phi$ , where  $v_s$  and

$v_w$  are, respectively, the specific volumes of the solution and water,

and where  $x_1$  and  $x_2$  are the weight fractions of water and solute. The apparent molal volume,  $\Phi$ , is obtained by multiplying  $\phi$  by  $M$ , the molecular weight of the solute.]

$\Phi_0$  = apparent molal volume at infinite dilution

$c$  = concentration [ moles per 1000 cc of solution;  $c = 1000/M(v_s/x_2)$  ]

$S$  = constant that varies with the salt

The relation often extends to concentrated solutions. We will also examine the relation that includes a  $c^{3/2}$  term in (1), an equation which has sometimes been found more adequate over greater concentration ranges.

On the assumption that Masson's equation (or its extensions) may be extrapolated to the solid state,<sup>1</sup> we can determine from the density data of the aqueous solutions of these salts the lattice distances of their crystal structures. The results for the alkali halides indicate that Masson's equation may be extrapolated to the condition approximating the crystalline salt. Within the limits of the validity of Masson's equation only the hypothesis that the crystal lattice structure is retained in solution, at least statistically, is pertinent.

## LATTICE STRUCTURES IN SOLUTIONS

In this paper, we intend to extend the range for the concept of a hypothetical volume in a solution at which the crystalline solid retains its lattice structure. Assuming that the crystal lattice structure is retained in solution, at least statistically, even to high dilutions, we will calculate the interionic distances for various concentrations.

We will now consider the feasibility of using Masson's relation to describe the lattice structures of the salts in solution. One interpretation of the hypothetical upper limit to the concentration of a solute in solution is given by Scott [ 2, 3] . He prefers to define this limiting volume by the "critical disruption volume,"  $V^*$  , which is established from the following considerations: In the crystalline state,  $R$  (the normal interionic distance of the lattice), is determined from the condition of the equilibrium of the attractive and repulsive forces of the ions. When the crystal is expanded from its normal equilibrium volume to  $V^*$  , the resulting cohesive forces

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<sup>1</sup>Masson suggested that this hypothetical upper limit was reached when the concentration of the electrolyte became the same as that of the pure crystalline salt [1]. A. F. Scott [2b] examines this in some detail.

reach a maximum; when this maximum force is exceeded the crystal is pulled apart, so the volume  $V^*$  marks the transition from the regular lattice arrangement to the more irregular and random arrangement in solution.

From a formula derived by Joffe [4],  $R^*$  (the interionic distance of the lattice in the "critical disruptive" state) is found, and from this  $V^*$  can be calculated. Scott then uses this value in Masson's equation to calculate  $\phi^*$ , the hypothetical maximum value of the apparent volume. It appears that for salts of the same crystal structure, the ratio  $k^* = \phi^*/V^*$  is essentially constant. In a subsequent paper by Rosen [5], these "critical disruptive volumes" were found by using only the specific volumes of the solutions and some assumptions about the mechanism of solution. An agreeable reconciliation between diverse ideas, this lends some support to the concept examined here in which Masson's relation is used to develop the idea of a lattice structure in solution.

## THE INTERIONIC ATTRACTION THEORY AND THE IONIC ATMOSPHERE

If we assume that Masson's equation describes the ionic solution up to the solid state (regardless of which views we adopt to mark this condition), we can infer from this relation that the concept of an ionic atmosphere can be precluded. It is possible to rewrite Masson's equation in the following form<sup>2</sup> (with the asterisk to denote the critical disruptive state):

$$\phi^* - \phi_0 = S(1000/V^*)^{1/2}. \quad (2)$$

Since  $V^*$ , and its corresponding  $\phi^*$ , designate some close-packed arrangement of ions in a crystal lattice structure, it cannot be said to describe a condition that is compatible with the idea of an ionic atmosphere. Similarly,  $\phi_0$ , the apparent volume at infinite dilution, precludes an ionic atmosphere because of the infinite separation of the ions at infinite dilution.

Thus, since the constant  $S$  in (2) is determined by the conditions at which the concept of an ionic atmosphere is untenable, it suggests, instead, that over the entire range of the validity of Masson's relation the geometry of the crystalline state is maintained. This is the basis for the concept of a statistical lattice structure in solution.

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<sup>2</sup>Where we have set  $V=M(v_s/x_2)$  in (1), in which  $x_2/v_s$  is the density of the solution and  $V$  is the molar volume.

This result may have an important relation to the theory of an ionic atmosphere in an electrolytic solution, an abstraction which might be replaced with our concept of a lattice structure in solution, as explained below.

Progress in developing the modern theory of ionic solutions has depended on several fundamental factors, namely, knowledge of the forces of attraction between ions and the distribution of these ions--two factors which are not mutually exclusive. With the formulation of appropriate distribution functions for the ions, and the supposed effects of these ions on each other, and with the use of specialized applications of the fundamental concepts of electrostatics, hydrodynamics, and statistical mechanics, exact theories have been developed which describe the properties of electrolytic solutions under some circumstances. The assumption of Coulomb forces between pairs of ions implies that the motion of ions is not entirely random--that the presence of an ion at a given point affects the spatial distribution of other ions in the immediate vicinity. Thus, for example, a positive ion will induce a negative charge density around it, and vice versa. This is the archetype of an "atmosphere" surrounding the ion, and this atmosphere can, on the average, contain more negative ions and fewer positive ions.

This is the concept of the ionic atmosphere. Beginning with its first successful use by Debye and Huckel, and amplified by the contributions of others, it led to the foundation of exact theoretical expressions on the interionic attraction theory of electrolytes.

The significance of this digression on the interionic attraction theory and the properties of the ionic atmosphere is the suggestion that a regular lattice structure, similar to that in the crystalline state, persists in solution. This idea may replace the concept of an ionic atmosphere.

## THE CALCULATION OF THE INTER IONIC DISTANCES IN SOLUTIONS

Masson's equation (1) may be written in the convenient form

$$\phi = a + b(x_2/v_s)^{1/2} \quad (3)$$

where a and b are constants characteristic of each salt and where the other quantities are as previously defined. The parameters a and b are determined by the least squares method by adapting the data for the specific volumes of the alkali halides for the data used.



Using (3), we have

$$k = a(x_2/v_S) + b(x_2/v_S)^{3/2} \quad (4)$$

where we have set

$$k = \phi(v_S/x_2) = 1 - v_W(x_1/v_S) \quad (5)$$

in the basic equation defining  $\phi$ . From (5) we see that there is a simple linear relation between  $k$  and  $(x_1/v_S)$ , the concentration of water.

In computing the interionic distances of the alkali halides, we have found it convenient to compare these distances for the same values of  $k$ , so that by virtue of (5) the interionic radii of the salts for the same water concentrations are available. This may readily be done for salts that have the same crystal structure.

The semi-cubic equation (4) is solved with suitable values of  $k$ , from which the molar volumes  $M(v_S/x_2)$ , corresponding to given water concentrations  $(x_1/v_S)$ , are determined. This has been done by an IBM 704 digital computer program that determines the least squares values of  $a$  and  $b$  in (3) and then solves (4) for the  $(x_2/v_S)$  value corresponding to the given  $k$ . (It is important to select the proper value of  $(x_2/v_S)$  if (4) has more than one real root.)

The interionic distance  $R$ , for the rock salt type<sup>3</sup> lattice structure, is computed from the relation  $R^3 = V/2N$ , where  $V = M(v_S/x_2)$ , or the molar volumes which are the roots of (4),  $N$  is Avogadro's number, and the factor  $1/2$  represents the number of molecules in the lattice cell.

In Table I the parameters for Masson's equations (1) and (3) are shown for aqueous solutions of the alkali halides<sup>4</sup>. In Table II are shown the interionic distances of the hypothetical crystalline salts of the alkali halides which are obtained from Masson's equation when the concentration is reached

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<sup>3</sup>The rock salt lattice structure is assumed for all the alkali halide salts, even where the body-centered type of structure might be expected. This choice is made both for simplicity and because there is evidence that in solution the former lattice type is more acceptable. (See Rosen [5], Table I.)

<sup>4</sup>Compare with Scott's values [2a, (p. 2317)]. Scott does not use a true least squares method for determining these parameters; he rejects more points (except for the lithium salts) than has here been found necessary.

TABLE I. THE PARAMETERS OF MASSON'S\* EQUATION FOR  
AQUEOUS SOLUTIONS OF THE ALKALI HALIDES\*\* AT 25° C

Salt	a	b	$\Phi_0$	S	Number of Points Rejected	Max $x_2$ Used
LiCl	0.4016906	0.1684250	17.03168	1.470467	2	0.11027
LiBr	0.2775638	0.0447647	24.10919	1.145948	2	0.19760
LiI	0.2663748	0.0151755	35.65427	0.7431423	4	0.19327
NaCl	0.2842798	0.1444299	16.61616	2.040957	0	0.25292
NaBr	0.2288073	0.0527981	23.54656	1.743028	0	0.39972
NaI	0.2339311	0.0234028	35.06628	1.358219	0	0.58748
KCl	0.3552161	0.1155451	26.48491	2.352395	0	0.21823
KBr	0.2839795	0.0463335	33.79924	1.902501	0	0.39951
KI	0.2727354	0.0242358	45.27680	1.639303	0	0.56073
RbCl	0.2641883	0.0517627	31.95093	2.177067	0	0.42537
RbBr	0.2342920	0.0301760	38.75190	2.029856	0	0.52552
RbI	0.2375125	0.0165882	50.44528	1.623680	0	0.40989
CsCl	0.2326763	0.0310573	39.17572	2.145662	0	0.65793
CsBr	0.2167073	0.0199496	46.12182	1.958771	0	0.53053
CsI	0.2229487	0.0108178	57.92654	1.432671	0	0.47766

\* The constants shown are for the expressions for the apparent specific volumes of the solute  $a + b(x_2/v_s)^{\frac{1}{2}}$  and the apparent molal volumes  $\Phi_0 + Sc^{\frac{1}{2}}$ , where  $c = 1000(x_2/v_s)/M$  is the molar concentration (moles per 1000 cc solution). The relations between these parameters are  $\Phi_0 = Ma$  and  $S = b(M^3/1000)^{\frac{1}{2}}$ .

\*\* Computed from the density data of G. P. Baxter and C. C. Wallace [7].

at which no water is present ( $k=1$ ). At this upper limit of the solution state, the apparent molar volume may be identified with the solid crystalline state. This view,<sup>5</sup> which appears reasonable from the data shown in Table II (except for the lithium salts), is, however, not essential to our argument--we are only concerned with discerning some evidence for a crystalline structure.

<sup>5</sup>Scott [2b], rejects this view and prefers to accept the "critical disruptive volume" as the upper limit to the solid crystalline state.

TABLE II. THE INTERIONIC DISTANCES OF THE  
CRYSTALLINE ALKALI HALIDES AT 25°C  
CALCULATED FROM THE DENSITY DATA OF THEIR SOLUTIONS<sup>a</sup>

	R (calc) <sup>b</sup>	R (calc) <sup>c</sup>	R (obs) <sup>d</sup>
LiCl	2.79	2.45	2.57
LiBr	2.94	2.86	2.75
LiI	3.20	3.21	3.03
NaCl	2.88	2.93	2.81
NaBr	3.02	3.02	2.98
NaI	3.26	3.26	3.23
KCl	3.17	3.20	3.14
KBr	3.29	3.30	3.29
KI	3.52	3.52	3.53
RbCl	3.28	3.31	3.29
RbBr	3.42	3.42	3.43
RbI	3.62	3.62	3.66
CsCl	3.44	3.44	3.46
CsBr	3.56	3.56	3.60
CsI	3.75	3.76	3.83

<sup>a</sup>The rock salt (NaCl) lattice structure is assumed for all the salts.  
See footnote 3.

<sup>b</sup>Computed from Masson's equation (3) whose parameters are shown in Table I and which were obtained by using the density data of G. P. Baxter and C. C. Wallace [7].

<sup>c</sup>Computed from the equation (6) whose parameters were determined by H. Zeldes. See [3].

<sup>d</sup>Values given by L. Pauling [8].

In Table III the specific volumes,  $(v_s/x_2)$ , of the aqueous solutions of the alkali halides are shown for various water concentrations  $(x_1/v_s)$ . In Table IV are shown the corresponding interionic distances on the assumption that the ions in solution retain a lattice structure. (See also Tables V and VI.)

Zeldes [3 (pp. 398 ff.); 6] has determined the parameters of the extended equation of Masson

$$\Phi = A + Bc^{1/2} + Cc^{3/2} \quad (6)$$

for each of fifteen alkali halides by the least squares method. He then determined the parameters of an equation of the same form as (6) for the eight individual ionic species. Empirical evidence on the additivity of the apparent ionic volumes requires that the sum of corresponding coefficients in (6) for the alkali and halide ions give the analogous coefficient of the binary solution. The result of these calculations is the demonstration that, within the experimental errors of the density data for the alkali halide solutions, the individual apparent ionic volumes appear to be additive over a wide concentration range.

Zeldes' values for the parameters of (6) for the alkali and halide ions, as well as the binary solutions, have been used here in a manner exactly analogous to that described above; (6) replaces Masson's relation (3) and a semi-quintic equation, instead of (4), is solved for the molar volumes  $M(v_s/x_2)$ . From the latter are determined the ionic radii of the ionic species (assuming an appropriate geometry for their lattice structures) in addition to the interionic distances for the alkali halide salts.

George C. Marshall Space Flight Center  
National Aeronautics and Space Administration  
Huntsville, Alabama, August 11, 1967  
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TABLE III. THE SPECIFIC VOLUMES,  $(v_s/x_2)$ , OF THE AQUEOUS SOLUTIONS OF THE ALKALI HALIDES AT 25°C OBTAINED FROM MASSON'S EQUATIONS\*

$x_1/v_s$ k	0 1.0	0.1 0.89971	0.2 0.79941	0.3 0.69912	0.4 0.59883	0.5 0.49853	0.6 0.39824	0.7 0.29795	0.8 0.19766	0.9 0.09736	0.95 0.047217	0.97 0.027158
LiCl	0.6162	0.6744	0.7464	0.8378	0.9581	1.1244	1.3700	1.7727	2.5644	4.9067	9.6554	16.3258
LiBr	0.3529	0.3884	0.4324	0.4886	0.5631	0.6667	0.8210	1.0764	1.5842	3.1115	6.2575	10.7237
LiI	0.2944	0.3256	0.3646	0.4147	0.4814	0.5745	0.7140	0.9464	1.4123	2.8286	5.7753	9.9853
NaCl	0.4905	0.5354	0.5907	0.6606	0.7527	0.8792	1.0652	1.3685	1.9602	3.6918	7.1636	12.0027
NaBr	0.3219	0.3531	0.3917	0.4410	0.5060	0.5961	0.7297	0.9498	1.3847	2.6812	5.3303	9.0706
NaI	0.2783	0.3070	0.3426	0.3883	0.4490	0.5335	0.6598	0.8694	1.2879	2.5531	5.1724	8.9026
KCl	0.5161	0.5656	0.6269	0.7049	0.8079	0.9503	1.1612	1.5080	2.1920	4.2257	8.3690	14.2084
KBr	0.3611	0.3973	0.4424	0.4999	0.5762	0.6822	0.8400	1.1013	1.6209	3.1834	6.4022	10.9717
KI	0.3159	0.3488	0.3897	0.4422	0.5120	0.6094	0.7549	0.9969	1.4806	2.9463	5.9861	10.3204
RbCl	0.3515	0.3862	0.4293	0.4843	0.5570	0.6579	0.8080	1.0558	1.5471	3.0194	6.0413	10.3211
RbBr	0.2903	0.3197	0.3563	0.4031	0.4651	0.5515	0.6802	0.8935	1.3183	2.5986	5.2412	8.9975
RbI	0.2695	0.2978	0.3331	0.3783	0.4385	0.5225	0.6481	0.8573	1.2759	2.5462	5.1846	8.9498
CsCl	0.2903	0.3197	0.3562	0.4028	0.4646	0.5507	0.6790	0.8913	1.3142	2.5881	5.2159	8.9498
CsBr	0.2561	0.2826	0.3155	0.3577	0.4137	0.4918	0.6084	0.8021	1.1890	2.3592	4.7829	8.2355
CsI	0.2448	0.2709	0.3035	0.3452	0.4008	0.4786	0.5950	0.7892	1.1784	2.3622	4.8262	8.3473

\* Obtained by solving the cubic  $k = \phi/(v_s/x_2) = a(v_s/x_2)^{-1/2} + b(v_s/x_2)^{-3/2}$  with appropriate values for k. The parameters a and b are shown in Table I, and were computed from the density data of Baxter and Wallace [7].

TABLE IV. THE INTERIONIC DISTANCES\* IN AQUEOUS ALKALI HALIDE SOLUTIONS AT 25°C  
COMPUTED FROM MASSON'S EQUATION

$(x_1/v_s)$ k	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.97
	1.0	0.89971	0.79941	0.69912	0.59883	0.49854	0.39824	0.29795	0.19766	0.09736	0.047217	0.027158
LiCl	2.79	2.87	2.97	3.09	3.23	3.41	3.64	3.97	4.49	5.57	6.98	8.31
LiBr	2.94	3.04	3.15	3.28	3.44	3.64	3.90	4.27	4.85	6.08	7.67	9.18
LiI	3.20	3.31	3.44	3.59	3.77	4.00	4.30	4.72	5.39	6.80	8.63	10.35
NaCl	2.88	2.96	3.06	3.18	3.32	3.49	3.73	4.05	4.57	5.64	7.03	8.35
NaBr	3.02	3.11	3.22	3.35	3.51	3.71	3.97	4.33	4.91	6.12	7.69	9.19
NaI	3.26	3.37	3.49	3.64	3.82	4.05	4.35	4.77	5.43	6.82	8.63	10.35
KCl	3.17	3.27	3.39	3.52	3.68	3.89	4.16	4.54	5.14	6.40	8.03	9.58
KBr	3.29	3.40	3.52	3.67	3.85	4.07	4.36	4.77	5.43	6.80	8.58	10.27
KI	3.52	3.64	3.77	3.94	4.13	4.38	4.70	5.16	5.89	7.41	9.38	11.25
RbCl	3.28	3.39	3.51	3.65	3.82	4.04	4.33	4.73	5.38	6.72	8.47	10.12
RbBr	3.42	3.53	3.66	3.81	4.00	4.23	4.54	4.97	5.66	7.09	8.96	10.73
RbI	3.62	3.74	3.89	4.06	4.26	4.52	4.85	5.33	6.08	7.66	9.71	11.64
CsCl	3.44	3.55	3.68	3.83	4.02	4.25	4.56	4.99	5.68	7.13	9.00	10.78
CsBr	3.56	3.68	3.82	3.98	4.18	4.43	4.76	5.21	5.94	7.47	9.45	11.33
CsI	3.75	3.88	4.03	4.21	4.42	4.69	5.04	5.54	6.33	7.99	10.13	12.17

\*Computed on the assumption that the lattice structure of the ions in solution is of the NaCl type. The equation used is  $M(v_s/x_2) = NR^3/f$ , where  $M(v_s/x_2)$ , the molar volume, is a cube of side R, f is the number of molecules per cube (which is 1/2 for the rock salt type), and where N is Avogadro's number. The specific volumes,  $(v_s/x_2)$ , used are from Table III.

TABLE V. THE SPECIFIC VOLUMES,  $(v_s/x_2)$ , OF THE ALKALI HALIDE IONS IN AQUEOUS SOLUTIONS AT 25° C\*

	$(x_1/v_S)^{**}$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.97	0.99
Li <sup>+</sup>	2.2686	2.3434	2.4285	2.5270	2.6431	2.7833	2.9582	3.1871	3.5102	4.0350	4.4792	4.7338	24.3167	
Na <sup>+</sup>	0.6205	0.6625	0.7128	0.7746	0.8526	0.9553	1.0979	1.3139	1.6922	2.6079	4.0242	5.5609	11.6705	
K <sup>+</sup>	0.5822	0.6288	0.6859	0.7577	0.8509	0.9778	1.1619	1.4572	2.0208	3.6139	6.6864	10.8448	36.5779	
Rb <sup>+</sup>	0.3114	0.3383	0.3715	0.4134	0.4682	0.5435	0.6539	0.8334	1.1819	2.1945	4.2091	7.0008	24.8335	
Cs <sup>+</sup>	0.2381	0.2607	0.2887	0.3243	0.3712	0.4360	0.5318	0.6892	0.9989	1.9171	3.7825	6.4064	23.4774	
Cl <sup>-</sup>	0.6418	0.7002	0.7730	0.8667	0.9915	1.1666	1.4297	1.8697	2.755	5.4602	11.1012	19.1668	72.6039	
Br <sup>-</sup>	0.3195	0.3537	0.3966	0.4518	0.5258	0.6298	0.7877	1.0547	1.5916	3.2312	6.6582	11.5690	44.2086	
I <sup>-</sup>	0.3088	0.3415	0.3824	0.4351	0.5053	0.6038	0.7517	0.9990	1.4964	3.0152	6.1869	10.7282	40.8782	

\*The results were obtained by solving the quintic  $k = \phi / (v_s/x_2) = a(v_s/x_2)^{-1/2} + b(v_s/x_2)^{-3/2} + c(v_s/x_2)^{-5/2}$  with appropriate values for k. The parameters a, b, and c are those determined by H. Zeldes: see [3], Table 8-9-1, p. 397.

\*\*

The corresponding values of k are shown in Table III.

TABLE VI. THE UNIT CELL LENGTHS\* OF THE ALKALI HALIDE IONS IN AQUEOUS SOLUTIONS AT 25° C

$(x_1/v_s)^{***}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.97	0.99	0.997
$\text{Li}^+$	2.36	2.38	2.41	2.44	2.48	2.52	2.57	2.64	2.72	2.85	2.96	3.01	5.19	9.87
$\text{Na}^+$	2.28	2.33	2.39	2.45	2.53	2.62	2.76	2.93	3.19	3.68	4.25	4.73	6.06	10.17
$\text{K}^+$	2.66	2.73	2.81	2.91	3.02	3.17	3.35	3.62	4.03	4.90	6.01	7.06	10.59	63.03
$\text{Rb}^+$	2.81	2.89	2.98	3.08	3.22	3.38	3.59	3.90	4.38	5.38	6.68	7.92	12.08	73.70
$\text{Cs}^+$	2.97	3.06	3.17	3.30	3.45	3.64	3.89	4.24	4.79	5.96	7.47	8.91	13.73	84.93
$\text{Cl}^-$	2.66	2.74	2.83	2.94	3.08	3.25	3.48	3.80	4.33	5.44	6.89	8.26	12.88	80.6
$\text{Br}^-$	2.77	2.86	2.97	3.11	3.27	3.47	3.74	4.12	4.72	5.99	7.62	9.16	14.31	89.84
$\text{I}^-$	3.19	3.30	3.43	3.58	3.76	3.99	4.29	4.72	5.40	6.82	8.67	10.42	16.27	10.20

\*The lattices for the unit cells for the ionic volumes are assumed to be of the rock salt (NaCl) type and were calculated from the specific volumes of the ions shown in Table V. The results are shown in Angstrom units.

\*\*The corresponding values of  $k$  are shown in Table III.



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